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Discrete wave mechanics: The hydrogen atom with angular momentum

(radial wave vectors/finite difference equations/threshold distances)

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ABSTRACT **A discrete wave mechanical treatment of the hydrogen atom is extended to deal with states involving nonzero angular momentum. Only the radial portions of the wave vectors are covered. It is predicted that there is a nonzero minimum distance between the electron and the nucleus; this threshold distance increases with increasing angular momentum. Appropriate finite difference equations are formulated. The states with angular momentum exhibit the same degeneracy as do corresponding energy levels obtained from solutions of Schrödinger's equation.**

In a recent article (1), I treated the quantum mechanical problem of a spherically symmetric hydrogen atom by using a discrete wave mechanical approach. This was done by solving a finite difference equation (instead of Schrödinger's equation), leading to solutions in the form of wave vectors (instead of wave functions). The formula for allowable energy levels, written explicitly for a newly defined "wave vector energy," looks just like the Bohr–Rydberg equation. The initial treatment was, however, limited to the hydrogen atom with zero angular momentum; this was done to avoid problems attending nonspherical symmetry.

To solve the more general problem—that involving angular momentum effects—would appear to require the development of discrete counterparts to the spherical harmonics. Unhappily, I have not yet succeeded in obtaining such discrete spherical harmonics in an exact form.* Nevertheless, it appears possible to establish the radial factors of the probability wave vectors and to see what, if anything, happens to the energy. It is my purpose in this paper to deal with that specific aspect of the discrete hydrogen atom problem. It is also my hope that someone, perhaps by using clues appearing in this article, will be able to develop a precise set of discrete spherical harmonics.

Search for a Complete Set of Discrete Radial Polynomials

To help us develop a general set of radial wave vectors for the hydrogen atom with angular momentum, let us first examine certain features of the differential equation treatment. When we tackle the problem with Schrödinger's equation, we use polar coordinates (r, θ, ϕ), thereby enabling us to separate the partial differential equation into three ordinary differential equations. The ϕ equation gives rise to a quantum number m, which then appears explicitly in the θ equation. The θ equation, in turn, brings out another quantum number, l, which appears explicitly in the r equation. Finally, the r equation leads to a third quantum number, n, upon which the energy depends.

In dealing with the problem in a discrete way, it seems reasonable that a not dissimilar procedure might work. However, if we do not know the θ equation and how it links to the r equation, how can we write down the radial equation with its dependence on l or a possible equivalent? A clue is forthcoming by examining the properties of the radial functions obtained from the differential equation (see, for example, ref. 2). That radial function looks like $[\exp(-\rho/2)]\rho^l L_{n+l}^{(2l+1)}(\rho)$, where ρ is proportional to r and $L_{n+l}^{(2l+1)}(\rho)$ is an associated Languere polynomial. But we also know specifically that

$$\frac{d^2}{d\rho^2} L_n^{(1)}(\rho) = L_{n'+1}^{(3)}(\rho), \quad [1]$$

where $n' = n - 1$. Therefore, if we know the polynomials for values of n with $l = 0$, we can readily get the polynomials for $l = 1$. Similarly, by using the polynomials for $l = 1$, we can obtain polynomials for $l = 2$, etc.

Now we already know the discrete polynomials for all values of n, if l or its equivalent is zero (1). Hence, if we take second differences of such, perhaps we can get valid discrete polynomials for $l \neq 0$. This can presumably be done not only for the polynomials but also for the finite difference equation from which the $l = 0$ solutions were obtained.

It was shown earlier (1) that discrete polynomials, comparable to the appropriate Languere polynomials for $l = 0$, are given, using previous notation, by the expression

$$G_{n,0}(\zeta) = F(\zeta)/\zeta = \sum_{k=0}^{n-1} \frac{(-1)^k(-n+1)_k(-\zeta+l)_k\gamma^k}{k!(k+1)!}, \quad [2]$$

where

$$\zeta = r/\Delta = rmc/\hbar, \quad [3a]$$

and

$$\mu = Ze^2/(\hbar c) = (n/2)[(1+\gamma)^{1/2} - (1+\gamma)^{-1/2}]. \quad [3b]$$

Upon taking l successive second differences of $G_{n,0}(\zeta)$, using for this purpose a second difference in the form $G_{n,0}(\zeta+1) - 2G_{n,0}(\zeta) + G_{n,0}(\zeta-1)$, we obtain an expression that, except for a constant multiplier that we shall omit, looks like

$$G_{n,l}(\zeta) = \sum_{k=0}^{n-l-1} \frac{(-1)^k(-n+l+1)_k(-\zeta+l+1)_k\gamma^k}{k!(2+2l)_k}. \quad [4]$$

$G_{n,l}(\zeta)$ is a variety of the Hahn polynomials (3). The integer n, as it appears in Eq. **4**, is actually less by an amount l from the n of Eq. **2**. This is a result of an adjustment that is necessary because a second difference reduces the principal quantum number, n, by 1 and increases l by 1. In other words, the n of Eq. **4** is the total quantum number of the final state in question and not the n of the starting equation.

Eq. **4** is valid only for values of $\zeta \geq l + 1$ and for $n \geq l + 1$. The requirement that ζ starts at a nonzero threshold value appears to have no immediate counterpart in the continuous solutions. We can, however, see a physical significance to

*I have obtained some approximations, but they lack the aesthetic preciseness one seeks in endeavoring to lock together discrete mathematical modules.

the threshold. Let us assume that, for discrete as well as for continuous representations, the total angular momentum of the electron is given by the familiar expression $[l(l+1)]^{1/2}\hbar$. Thinking in pseudoclassical terms and using a wave vector kinetic energy expression (4), we can calculate the electron velocity at the perihelion of a trajectory† as follows:

$$\begin{aligned}\mathcal{T} &= mv^2/2 \\ &= l(l+1)\hbar^2/(2mr^2) \\ &= l(l+1)mc^2/2\zeta^2.\end{aligned} \quad [5]$$

From this we see that, if $\zeta = l$,

$$v = (1 + 1/l)^{1/2}c. \quad [6]$$

Since this value of v is larger than c, we conclude that the electron cannot get that close to the nucleus. On the other hand, for $\zeta = l + 1$, we find

$$v = (1 + 1/l)^{-1/2}c, \quad [7]$$

a quantity less than c and, hence, permissible. The foregoing arguments appear to be fully consistent with the wave vector energy concept set forth earlier (4). The wave vector energy must always be less than $mc^2/2$ and group velocities must be less than c.

More General Radial Difference Equations

Although Eq. **4** provides us with the desired polynomials, we would also like to find an equation for which the polynomials are solutions. Such a difference equation can be obtained by manipulating the equation whose solutions are $G_{n,0}(\zeta) = F(\zeta)/\zeta$. The equation for $G_{n,0}(\zeta)$ is found from that for $F(\zeta)$ to be (1)

$$(1+\gamma)^{1/2}(\zeta - 1)G_{n,0}(\zeta - 1) - 2(\lambda - \mu/\zeta)\zeta G_{n,0}(\zeta) + (1+\gamma)^{-1/2}(\zeta + 1)G_{n,0}(\zeta + 1) = 0. \quad [8]$$

Upon taking l successive second difference of the whole of Eq. **8**, we find after simplification that

$$(1+\gamma)^{1/2}(\zeta - l - 1)G_{n,l}(\zeta - 1) - 2(\lambda - \mu/\zeta)\zeta G_{n,l}(\zeta) + (1+\gamma)^{-1/2}(\zeta + l + 1)G_{n,l}(\zeta + 1) = 0. \quad [9]$$

In Eq. **9**, the number n is less by l than the n of Eq. **8** for reasons explained earlier in connection with Eqs. **2** and **4** The derivation described would actually appear to replace μ by $\mu(n - l)/n$. The factor $(n - l)/n$ must be suppressed, however, in light of Eq. **3b**, since successive second differences reduce the original n by l to give the final n. The form of Eq. **3b** stays intact, with μ constant and γ a function of n. Although n does not appear explicitly in the three coefficients of Eq. **9**, it is implicit by reason of Eq. **3b**. It can now be established by direct substitution that the expression of Eq. **4** will satisfy Eq. **9** provided

$$\begin{aligned}2\lambda &= (1+\gamma)^{1/2} + (1+\gamma)^{-1/2} \\ &= 2(1 + \mu^2/n^2)^{1/2}.\end{aligned} \quad [10]$$

The wave vector energy, $\mathcal{E}_n$, is given by

$$\begin{aligned}\mathcal{E}_n &= (mc^2/2)(1 - \lambda^2) = -mc^2\mu^2/(2n^2) \\ &= -2\pi^2 mZ^2e^4/(n^2h^2).\end{aligned} \quad [11]$$

†This should not be considered a fixed orbit like that of Bohr.

It is clear that the energy levels are degenerate and, as far as l is concerned, such degeneracy is precisely the same as for the solutions of Schrödinger's equation. Finally, the degenerate energy expression (Eq. **11**) looks like the Bohr–Rydberg equation, except for the use of m in place of m_0.

Although we appear to have satisfactory discrete polynomials, the complete radial wave vector still requires two more factors if it is to resemble $[\exp(-\rho/2)]\rho^l L_{n+l}^{(2l+1)}(\rho)$, as obtained from the differential equation. The exponential factor poses no problem; it must be $(1+\gamma)^{-\zeta/2}$. On the other hand, we cannot simply use ζ^l for the other factor; surely it must be some kind of discrete *l-th* degree power of ζ.

An acceptable factor can be found by judicious guesswork followed by trial and error. The overall weighted wave vector, corresponding to $r\psi(r)$ is found to be given by $\phi(\zeta)$ where

$$\phi(\zeta) = (1+\gamma)^{-\zeta/2}[(\zeta - l)/2]_{l+1}G_{n,l}(\zeta). \quad [12]$$

The factor $[(\zeta - l)/2]_{l+1}$, which is the same as $(\zeta - l)(\zeta - l + 2)\ldots(\zeta + l - 2)(\zeta + l)/2^{l+1}$, is actually of degree $l + 1$ instead of l. This accommodates the geometric weight factor, like the factor r of $r\psi(r)$, to render the square of $\phi_{n,l}(\zeta)$ proportional to the probability of finding the electron at a distance $\zeta\Delta$ from the proton.

Upon replacing $G_{n,l}(\zeta)$ in Eq. **9** by $\phi_{n,l}(\zeta)$, by using Eq. **12**, we obtain

$$\phi(\zeta - 1) - (\lambda - \mu/\zeta)\{[(\zeta - l + 1)/2]_l/[(\zeta - l)/2]_{l+1}\}\zeta\phi(\zeta) + \phi(\zeta + 1) = 0. \quad [13]$$

Unless the electron is close to the nucleus, ζ will be large compared to l. For large values of ζ, we can write

$$\zeta\{[(\zeta - l + 1)/2]_l/[(\zeta - l)/2]_{l+1}\} = 2 + l(l+1)/\zeta^2 + \ldots. \quad [14]$$

The term $l(l+1)/\zeta^2$ is precisely what is needed to transform Eq. **13** by a limit process into the ordinary differential equation for the radial part of the continuous wave function.

Discussion

Ordinarily, when working on a theoretical problem, one starts with some basic equation and seeks a solution applicable to the specific problem on hand. In some respects, the treatment in this paper is much the reverse. We quickly found what looked like good discrete radial polynomials applicable to states of the hydrogen atom possessing angular momentum. Next, we hunted for a difference equation from which those polynomials might be obtained. This was followed by embellishing the polynomials with other factors to obtain an overall radial wave vector. Finally, we found an equation for which those radial wave vectors are solutions.

At this juncture, however, we might properly ask: how good are those equations? Now we do know that the difference equations and their solutions, as presented in this paper, all reduce to some familiar differential equations and continuous functions as $c \to \infty$ (which makes $\Delta \to 0$). Such limit equations are shown in the *Appendix*. Although we get, through the limit process, the expected continuous expressions, this does not prove that the discrete equations are correct; after all, there are an infinite number of difference equations that can become a particular differential equation. Nevertheless, there are some unique features of the discrete treatment presented here that are attractive. The threshold value for the smallest possible separation of the electron from the proton is an example. This conclusion arose quite naturally and looks most reasonable, even though it vanishes as $\Delta \rightarrow 0$. The energy relations are likewise highly satisfactory without requiring approximations or recourse to asymptotic behavior.

It is my hope that Eq. **13** will be helpful in obtaining a θ equation. We can see from Eq. **14** that there is some promise. The rotational wave vector energy, $\mathcal{E}_{\mathrm{rot}}$, divided by mc^2, will approximately look much like

$$\frac{\mathcal{E}_{\mathrm{rot}}}{mc^2} = \frac{l(l+1)}{2\zeta^2} = \frac{l(l+1)\Delta^2}{2r^2} = \frac{l(l+1)\hbar^2}{2Imc^2}, \quad \textbf{[15]}$$

where I is a moment of inertia. Hence the discrete counterpart of ζ^l does seem to tell us something about how the θ equation will mesh with the ζ equation. From this we might well be able to formulate a set of discrete spherical harmonics. For this purpose it should prove helpful to recognize that in essence

$$\lambda = \lambda_r \lambda_\theta \lambda_\phi. \quad \textbf{[16]}$$

In other words, the separation of variables should involve factoring of λ, while retaining cognizance of relativistic energy considerations.

Appendix

The discrete equations and expressions in the main text can be reduced to continuous forms by letting $c \rightarrow \infty$. Some of these continuous formulations are listed below. If previously numbered equations are involved, they are given the same numbers as before but are preceded by the letter **A**.

If $\rho = 2m_0Ze^2r/(n\hbar^2)$, then

$$\lim_{c\rightarrow\infty} \gamma\zeta = \rho,$$

$$\lim_{c\rightarrow\infty} (1+\gamma)^{-\zeta/2} = \exp(-\rho/2),$$

and

$$\lim_{c\rightarrow\infty} G_{n,l}(\zeta) = \sum_{k=1}^{n-l-1} \frac{(-n+l+1)_k\rho^k}{k!(2+2l)_k}. \quad \textbf{[A4]}$$

Also,

$$\rho G''(\rho) + [2(l+1) - \rho]G'(\rho) + [n-l-1]G = 0, \quad \textbf{[A9]}$$

$$\lim_{c\rightarrow\infty} \phi(\zeta) = \exp(-\rho/2)\rho^{l+1}L_{n+l}^{(2l+1)}(\rho), \quad \textbf{[A12]}$$

and

$$\phi''(\rho) + [-1/4 + m/\rho - l(l+1)/\rho^2]\phi = 0. \quad \textbf{[A13]}$$

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